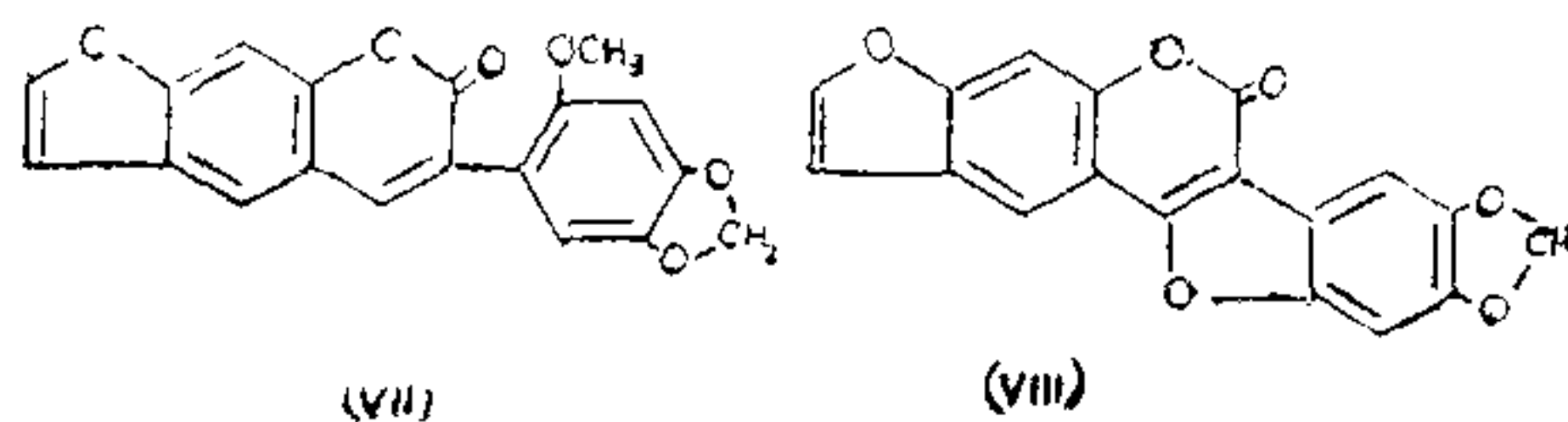


CHEMICAL COMPONENTS OF YAM BEANS: THEIR EVOLUTION AND INTERRELATIONSHIP

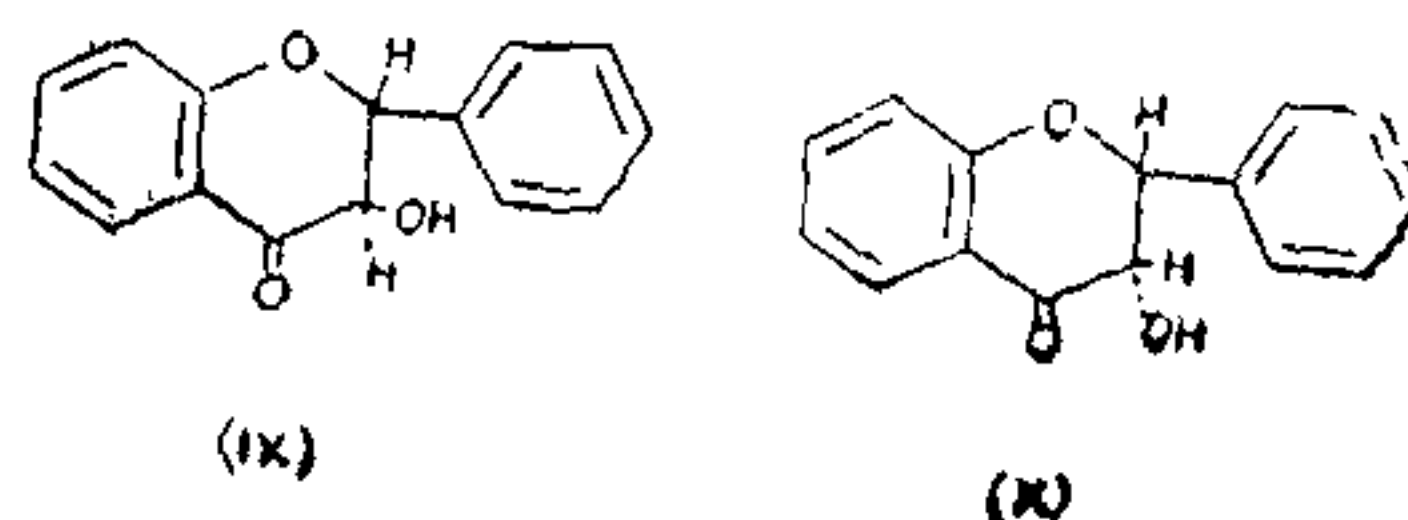
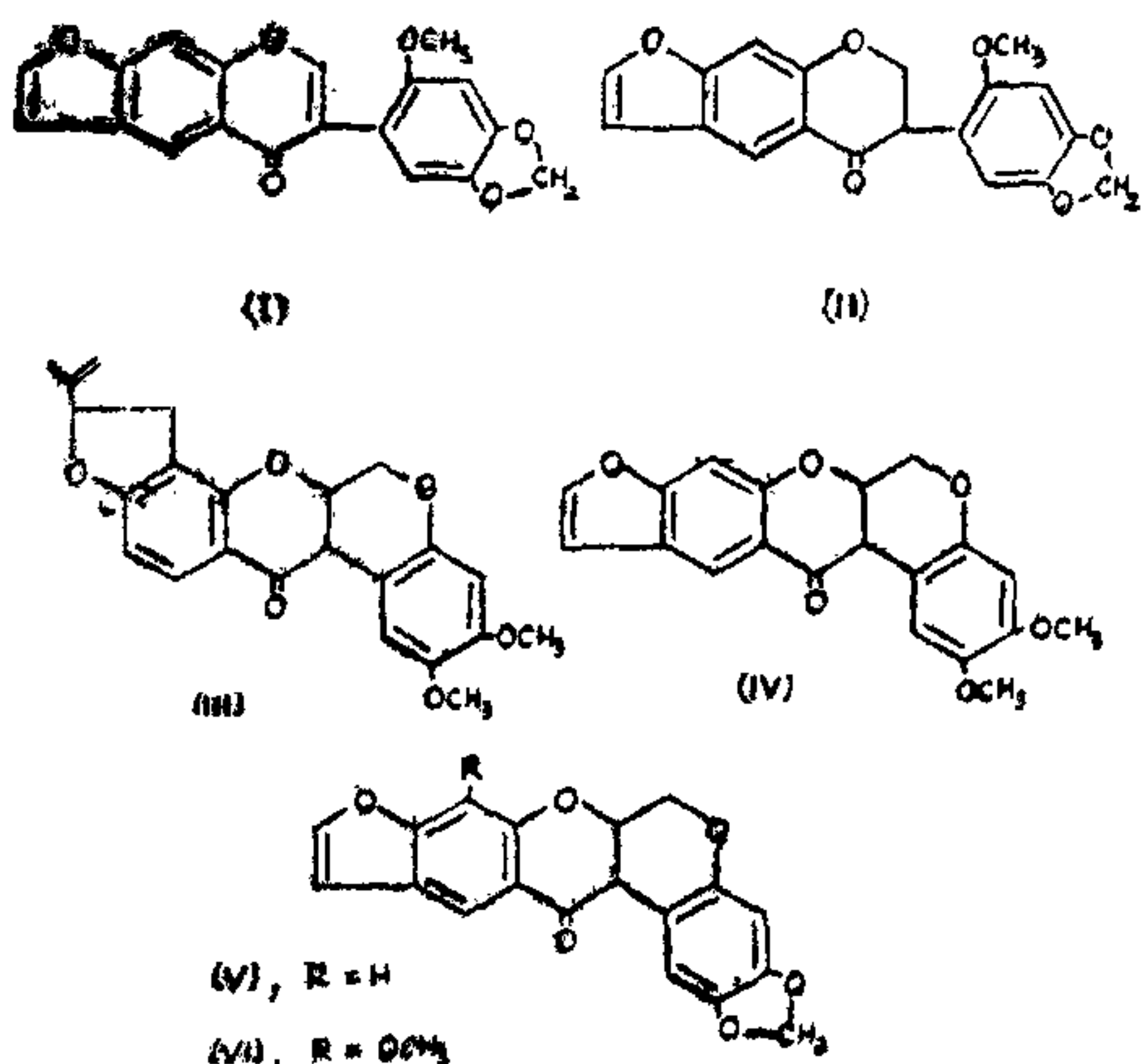
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PACHYRRHIZUS EROSUS (Sankh alu) is cultivated throughout India, but not known in a wild state. The tuberous root resembles a turnip in taste and consistence. It is eaten both raw and boiled. The seeds are toxic and the toxicity is comparable to that of the rotenone bearing roots of *Derris* and *Lonchocarpus*. The earliest study of the seeds was made by Nag et al.,¹ who considered the toxic principle to be a saponin. A more detailed examination was carried out by Norton and Hansberry² who isolated six crystalline compounds from them. One of these was identified as rotenone (III) and the second designated as erosone (IV) was shown to be closely related to elliptone and was its linear isomer; in it the furan ring is linearly fused whereas in elliptone it is angular. The structures of three more were determined by Schmid and his colleagues. These were pachyrrhizin³ (VII), erosnin⁴ (VIII) and pachyrrhizone⁵ (VI). The sixth compound was identified as dehydroneotenone (I) by Crombie and Whiting⁶ who also established the presence of two more, dolineone (V) and neotenone (II). Thus the seeds of *Pachyrrhizus erosus* contain eight closely related compounds; an isoflavone (I), an isoflavanone (II), four rotenoids (III, IV, V and VI) and two furano-3-phenyl coumarins (VII and VIII). The isolation of these from the same plant is of considerable biogenetic interest.



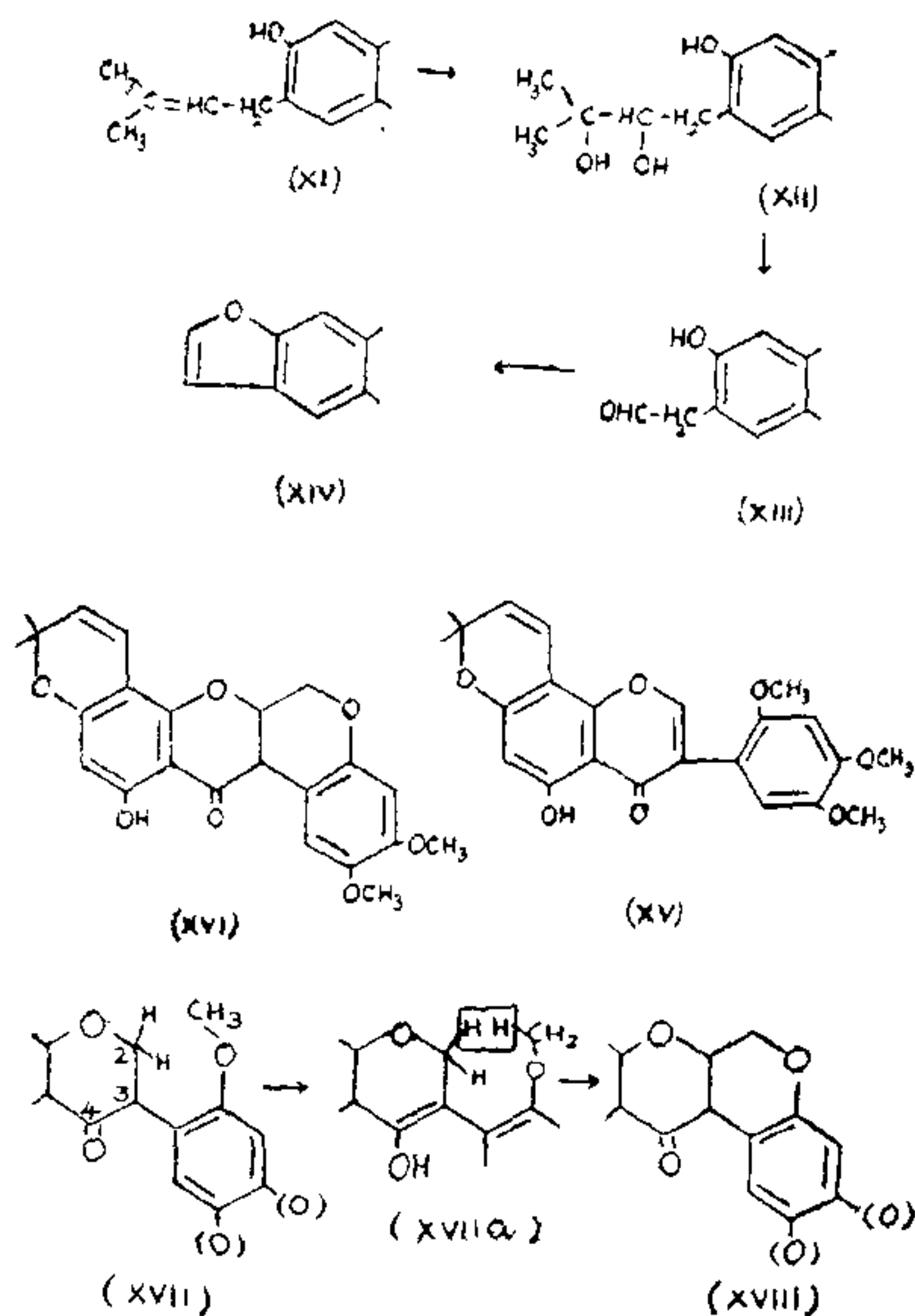
It is clear that the three types are closely related with the same carbon skeleton and very similar substitution patterns. There is no doubt that they have common origin and somewhat common evolution and have diversified in the end stages. The following comments may be made about the interrelationships and possible stages of evolution. The simplest of these compounds are the isoflavone (I) and isoflavanone (II). These are hydrogenation and dehydrogenation products. The evolution of isoflavones has already been discussed.⁷ There seems to be little doubt that they arise from chalcones which can easily isomerise into flavanones. It has been recently mentioned that flavanones, and not the 3-hydroxy flavanones, give rise to isoflavones.⁸ This point may require reconsideration. The more stable *trans*-3-hydroxyflavanones (IX) may not undergo this change. However it is quite possible that the less stable *cis*-3-hydroxyflavanones (X) may easily eliminate water and in the process undergo conversion into isoflavones.



The evolution of furan ring has also been discussed and established elsewhere.⁹ The origin seems to be a dimethylallyl unit which undergoes oxidative splitting off three carbon atoms with subsequent ring closure (see XI to XIV). The furan ring is present in all the eight compounds of yam beans. The above scheme of biogenesis is substantiated by the presence of a C₅ unit intact in one of the compounds, viz., rotenone.

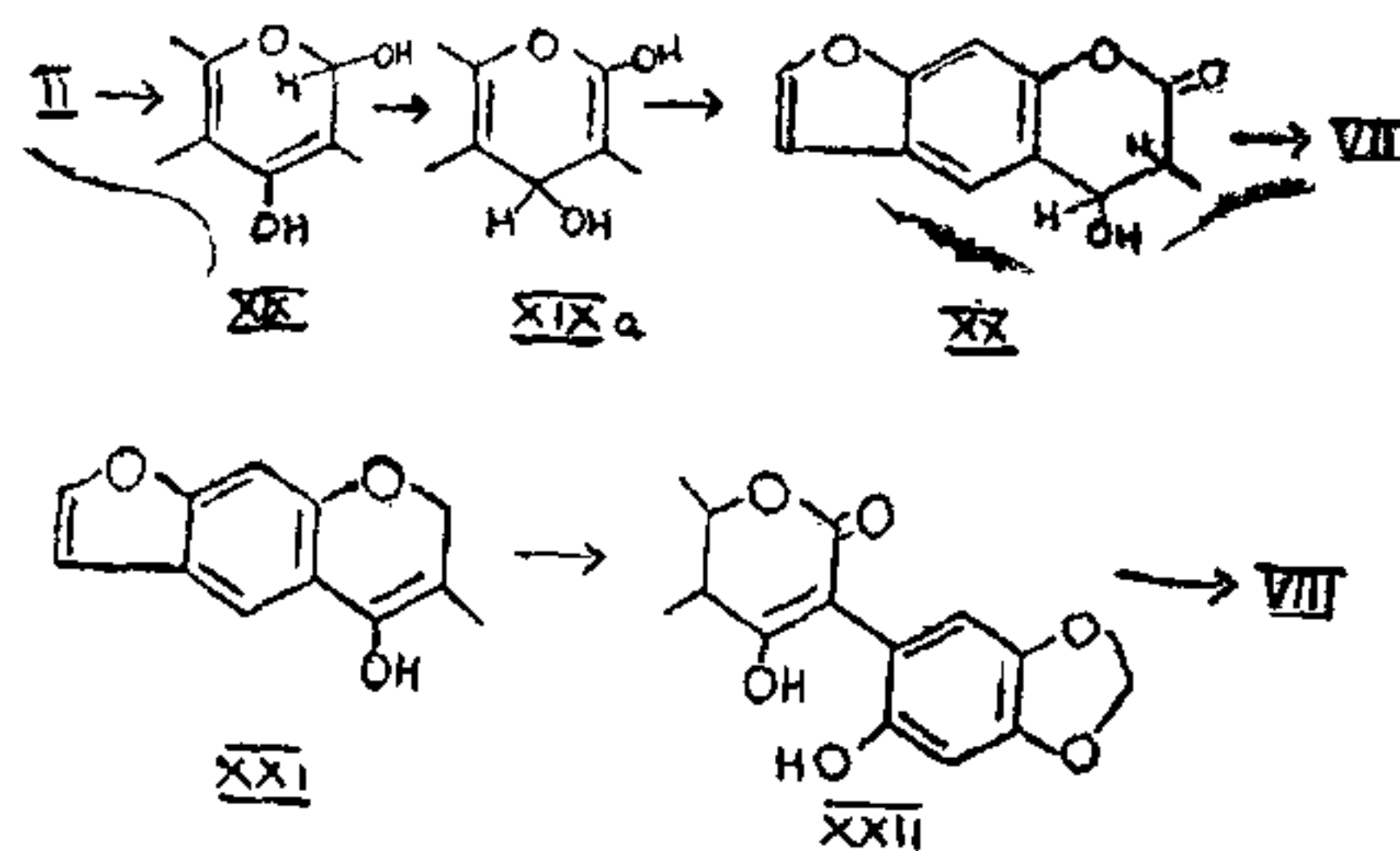
The occurrence of a 2'-OCH₃ substituted isoflavone (dehydroneotenone, I) and isoflavanone (neotenone, II) along with dolineone is a

second example of the co-occurrence of an isoflavonoid with a related rotenoid. The first was toxicarol isoflavone (XV) which is found along with toxicarol (XVI) in *Derris malaccensis*.¹⁰ These examples would suggest that the formation of the pyran ring may consist of a simple transformation involving possibly a free radical oxidation between the $-\text{CH}_2$ group in the 2-position and the $-\text{OCH}_3$ at the 2'-position. An analogy for this idea is the formation of methylenedioxy compounds from guaiacol units by this process of oxidation.¹¹ In the present case the 2-position can become more reactive by assuming the enol form (see XVII a).

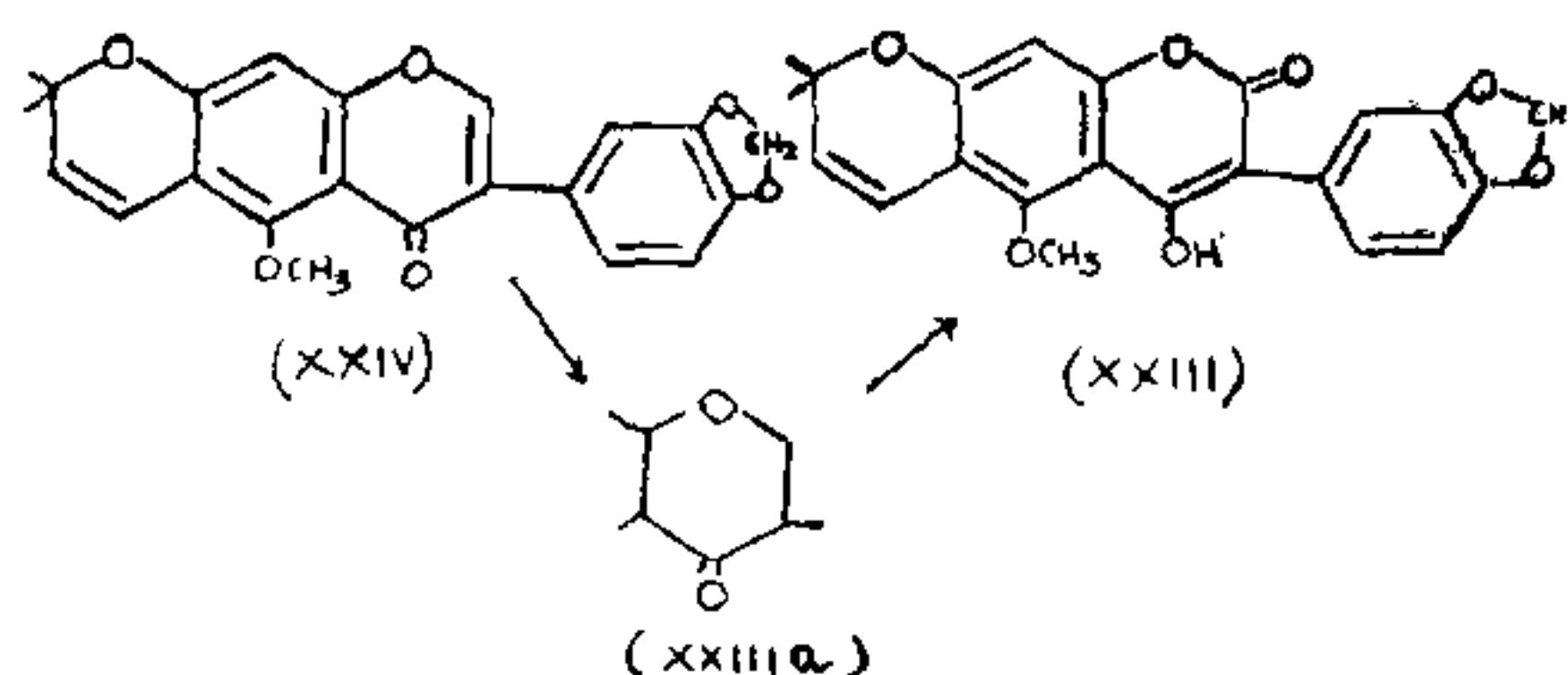


The close structural relationship between the two coumarin derivatives, pachyrrhizin and erosin, is obvious. They should therefore have very closely similar paths of biogenesis also originating from isoflavones and isoflavanones. It appears quite possible that oxidation in the 2-position of the isoflavanone (II) (enol form) without involving ring closure may lead to a 2'-hydroxyisoflavanone (XIX) which undergoes allylic isomerisation to the corresponding coumarin derivative (XX) followed by dehydration yielding the simpler 3-phenyl coumarin (VII). Somewhat similar changes are involved in the formation of (VIII) but in this case the presence of a free 2'-hydroxyl should make the difference. The steps would be the formation of

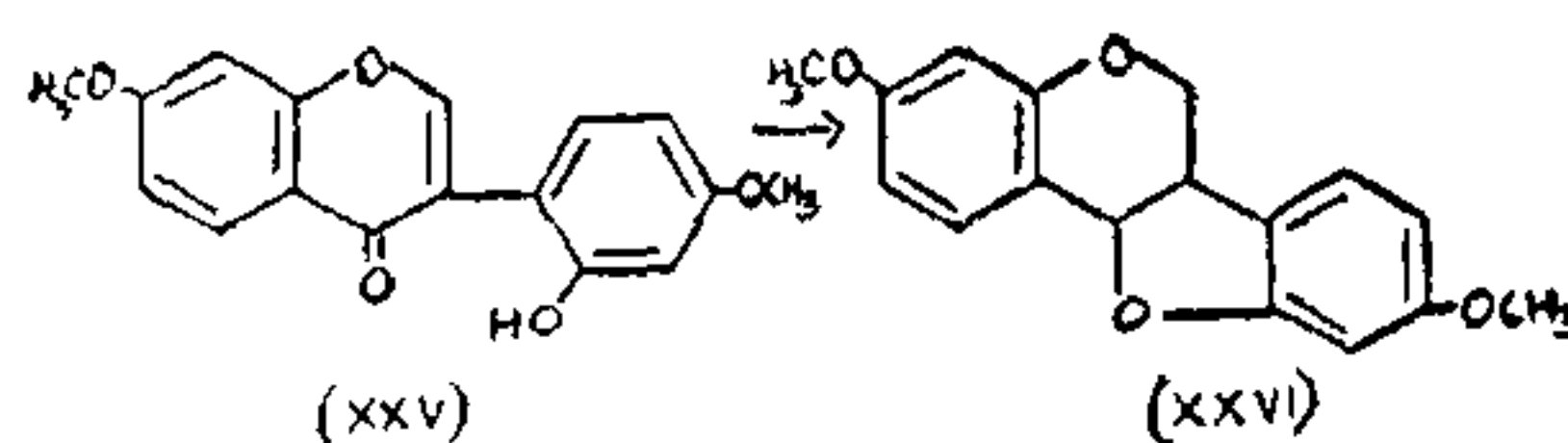
the enol (XXI) hydroxylactone (XXII) and ring closure.



In this connection could be recounted the presence of rotenoids and non-rotenoids in related *Derris* species. The non-rotenoids¹² in these cases are the 3-phenyl-4-hydroxy coumarins (e.g., XXIII) having no substitution in the 2'-position. This absence would explain their ready formation from isoflavones (XXIV) which accompanies them and also the lack of further change.¹³

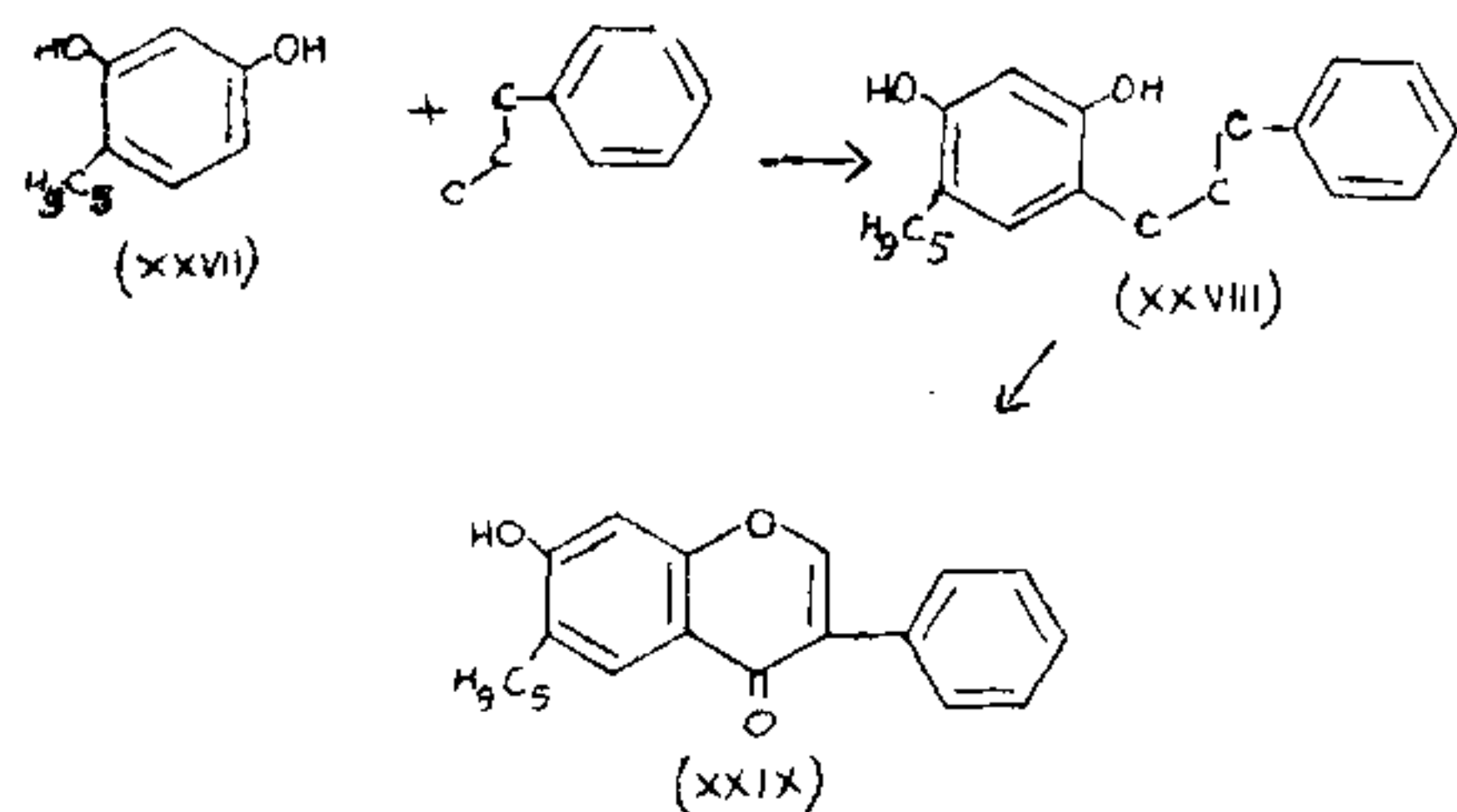


The formation of pterocarpin type which are common in the heartwood of pterocarpus species is obviously due to a slightly different method of evolution where 2'-hydroxy isoflavanone undergoes reductive ring closure. This has been confirmed by laboratory experiments and a number of compounds of this type have been made¹⁴ by reducing the appropriate isoflavones with sodium borohydride.



A special feature with seven out of the eight compounds of *Pachyrrhizus erosus* is that they all have a linearly fused furan ring; the only exception is rotenone. It is known that the entry of a dimethylallyl group takes place preferentially in the 8-position in flavonoids and a corresponding position in the related resacetophenone derivatives. The formation of

the linear compounds would involve entry of this unit in the position corresponding to 6. This would be possible if in these cases a C_5 unit got attached to the original C_6 component of the flavonoid before it was linked with the C_9 component.



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ANALYSIS OF PHENOL, HYDROQUINONE, QUINONE AND MALEIC ANHYDRIDE IN A MIXTURE

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THE study of catalytic vapour phase oxidation of benzene involves the problem of estimating phenol, hydroquinone, quinone and maleic anhydride in a mixture of all these along with unreacted benzene. Though there are a number of methods for the estimation of the individual compounds, there has been no report of any detailed work pertaining to the interferences by the other compounds present while estimating each of these in a mixture. Denton *et al.*¹ as well as Marisic² in their studies on the oxidation of aromatic compounds have employed a procedure involving separation of the compounds and subsequent analysis of them individually. However, it is preferable to estimate each constituent in a mixture as such than employ a quantitative separation followed by individual estimation. With this in view, synthetic mixtures containing known amounts of phenol, hydroquinone, quinone and maleic anhydride were prepared and a procedure for estimating the compounds was evolved after extensive testing.

A large number of methods of estimating phenol are based on the bromination of phenol followed by determination of the excess reagent. Phenol being acidic can also be determined by alkalimetric titration. However, in presence of carboxylic acids such estimations are not possible. Also the highly sensitive colorimetric method cannot be employed here since the presence of even small amounts of quinone and hydroquinone will modify the characteristic phenol colouration considerably.³ Hence bromination method was adopted here for the estimation of phenol in these synthetic mixtures. The bromination was carried out using bromate-bromide reagent.⁴

Reagents :

- (i) 0.1 N sodium thiosulphate solution prepared by dissolving 24.8 g. of $Na_2S_2O_3 \cdot 5H_2O$ in one litre of water.
- (ii) Brominating solution consisting of 3.5 g. of potassium bromate and 55 g. of potassium bromide in one litre of solution.